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Second Example of a Cubane-Like Nickel(II) Complex in a Series of N-Derivatives of Taurine

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Abstract—A new homometallic cubane-like nickel(II) complex based on *N*-2-(2-pyridyl)ethyl-2-aminoethanesulfonic acid $[Ni_4L_4(OH)_4]\cdot 2H_2O$ (**I**) is synthesized, and its structure is studied by X-ray diffraction (XRD) (CIF file CCDC no. 2211359). In crystals of the complex, the metallocenters are joined into tetrahedra with the Ni...Ni distances (3.144–3.201 Å) supplemented to cubanes by the μ_3-bridging oxygen atoms of the hydroxy groups. The coordination environment of each metallocenter is a distorted octahedron. The ligand is deprotonated, exists in the facial conformation, and performs the tridentate function to form two six-membered conjugated chelate cycles.

Keywords: cubane-like nickel(II) complex, N-derivatives of taurine, complex formation, XRD
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INTRODUCTION

The methodology of target synthesis of coordination compounds is predetermined by understanding the influence of the polydentate ligand structure on the structure of the complex [1]. Several donor atoms in the ligands provide possibilities for the formation of complexes with diverse structural features and properties [1]. Amino acids are the key participants of exchange processes that occur in all living organisms, and their derivatives being efficient chelating agents [1–5] can find use in metabolism regulation of metal ions, including nickel, in plants. Along with the general toxic effect observed at high concentrations of nickel ions, which is manifested as the inhibition of mitotic and enzymatic activities in water disbalance, photosynthesis, nitrogen metabolism [6], and oxidative stress induction [7], the physiological role of nickel ions, as of many other metal ions, for higher plants is the involvement in metabolism during the whole living cycle. Nickel ions are components of plant enzyme hydrogenases and ureases and, hence, their low concentration in plant tissues induces nitrogen metabolic disturbance and urea accumulation in concentrations hazardous for plants [6], which results in cell damage and, in ultimate cases, in plant decay. Many molecule-targets are known, whose activity can be inhibited by nickel ions, which induces chlorosis, necrosis, inhibition of shoot and root elongation, and a decrease in the leaf surface area [6].

In addition, the nickel complexes based on sulfur- and amino-containing Schiff bases demonstrate antibacterial, antiviral, and anticancer properties [8]. The preparation of new nickel complexes based on S-bearing amino derivatives is important for understanding the formation, stability, and role of the S-containing coordination sites in the metalloenzymes [9, 10] and for evaluating specific features of the behavior of the Ni-containing enzymes in various media [11]. Thus, taking into account the important role of the nickel(II) coordination compounds in the vital activity of living organisms and a possibility of synthesizing polynuclear complexes based on 2-pyridylmethyl-containing ligands [8, 12], we believe that the synthesis of new coordination compounds with the N-derivatives of amino acids and evaluation of their biological activity are important tools for the preparation of novel phytohormonal agents.

This work is a continuation of the cycle of studies of the complexation properties of N-derivatives of β-alanine [1, 4, 5, 12] and its structural analog taurine [2, 3] and demonstrates the possibility of the synthesis of the cubane-like nickel(II) complex $[Ni_4L_4(OH)_4]\cdot 2H_2O$ (**I**) based on *N*-2-(2-pyridyl)ethyl-2-aminoethanesulfonic acid (HL).

EXPERIMENTAL

All reagents were purchased from Sigma-Aldrich and used as received. ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer relatively to TMS using D_2O as the solvent. Elemental analysis was car-

ried out on a Perkin Elmer CHN PE 2400 automated analyzer. The nickel content was determined by atomic emission spectroscopy on an iCAP 6300 Duo spectrometer. FT-IR spectra were measured on a Spectrum Two spectrometer (Perkin Elmer) equipped with an attenuated total internal reflectance (ATR) accessory with a diamond crystal.

Synthesis of *N*-2-(2-pyridyl)ethyl-2-aminoethanesulfonic acid (HL). A mixture of 2-vinylpyridine (5.28 mL, 0.05 mol) and 2-aminoethanesulfonic acid (6.25 g, 0.05 mol) in water (30 mL) was hold at 70°C for 24 h. Water was evaporated on a rotary evaporator, ethanol (50 mL) was added to the residue, and the resulting mixture was brought to boiling and cooled to −18°C. The residue was filtered off and dried at 20°C to a constant weight. The yield was 9.43 g (82%).

For $C_9H_{14}N_2O_3S$

Anal. calcd., %	C, 46.96	H, 6.09	N, 12.17	S, 13.91
Found, %	C, 47.39	H, 6.53	N, 11.97	S, 13.01

^{1}H NMR (D_2O; δ, ppm): 3.23 (t, 2H, J = 6.4 Hz, $CH_2CH_2SO_3$); 3.27 (t, 2H, J = 5.6 Hz, CH_2CH_2N); 3.29 (t, 2H, J = 6.4 Hz, CH_2SO_3); 3.53 (t, 2H, J = 5.6 Hz, CH_2CH_2N); 7.37 (d, 1H, J = 4.0 Hz, α-*H*Py); 7.40 (t, 1H, J = 6.0 Hz, β-*H*Py); 7.85 (d, 1H, J = 6.0 Hz, β'-*H*Py); 8.50 (td, 1H, J = 6.0 Hz, 1,2, γ-*H*Py).

Synthesis of tetrakis(μ$_3$-hydroxo-*N*-(2-(2-pyridyl)ethyl)-2-aminoethanesulfonato)tetranickel(II) dihydrate (I). Weighed samples of HL (0.33 g, 1.6 mmol) and sodium hydroxide (128 mg, 3.2 mmol) were dissolved in water (5 mL), the solution was mixed with a solution of nickel nitrate hexahydrate (0.47 g, 1.6 mmol) in water (5 mL), and crystallization was carried out at 20°C with the slow evaporation of the solvent. The precipitate was filtered off and dried at 20°C to a constant weight. The yield was 90%.

For $C_{36}H_{56}N_8O_{16}S_4Ni_4 \cdot 2H_2O$

Anal. calcd., %	C, 34.39	H, 4.78	N, 8.92	S, 10.19	Ni, 18.79
Found, %	C, 33.88	H, 5.01	N, 9.15	S, 10.04	Ni, 19.12

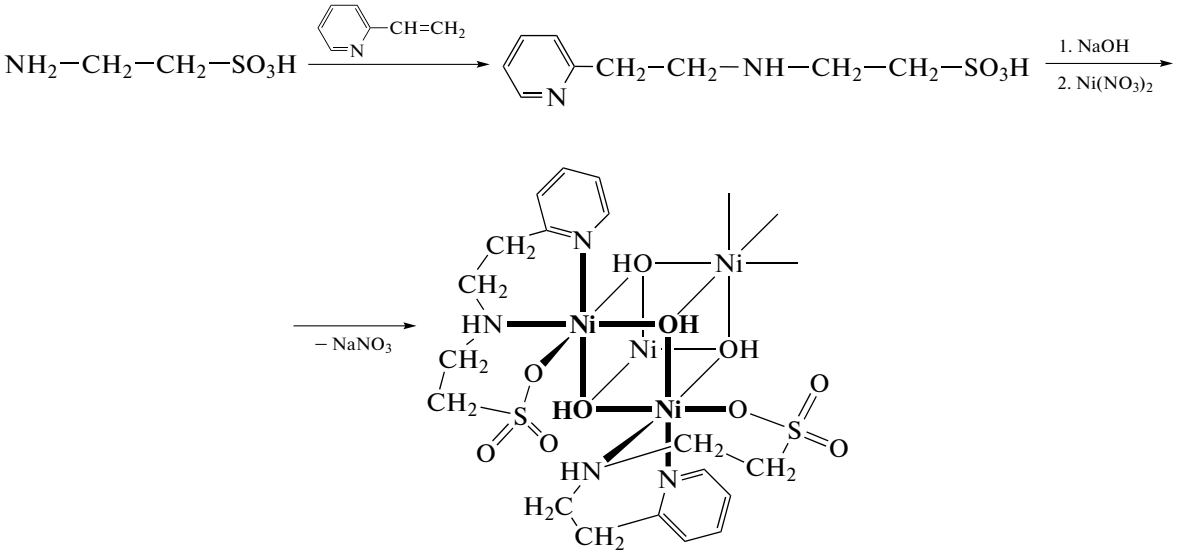
XRD. The experimental data for complex **I** were obtained on an Xcalibur 3 automated diffractometer (CCD detector, MoK_α, λ = 0.7107 Å, graphite monochromator) at T = 295(2) K. An empirical absorption correction was applied [13]. The structure was solved and refined using the SHELX software [14]. All non-hydrogen atoms were solved by a direct method and refined in the anisotropic approximation, and hydrogen atoms were placed in geometrically calculated positions and included in refinement by the riding model with dependent thermal parameters. The crystallographic data and experimental structure refinement characteristics are given in Table 1.

The coordinates of atoms and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2211359; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The aza-Michael reaction of direct addition of taurine to 2-vinylpyridine in water was used for the synthesis of the *N*-2-(2-pyridyl)ethyl-2-aminoethanesulfonic acid ligand (HL). The ^{1}H NMR and FT-IR spectra of HL are shown in Figs. 1 and 2, respectively.

Complex $[Ni_4L_4(OH)_4]\cdot 2H_2O$ (**I**) was prepared by the subsequent treatment of sodium salt of compound HL with nickel(II) nitrate (Scheme 1). The composition and structure of complex **I** were proved by XRD.



Scheme 1.

Table 1. Crystallographic data and experimental and structure refinement parameters for complex **I**

Parameter	Value
Molecular formula	$C_{36}H_{60}N_8O_{18}S_4Ni_4$
FW	1256.00
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a, Å	12.4877(7)
b, Å	19.7446(11)
c, Å	20.0700(14)
α, deg	90.00
β, deg	91.471(6)
γ, deg	90.00
V, Å^3	4946.9(5)
ρ_{calc}, g/cm^3	1.686
μ, mm^{-1}	1.747
F(000)	2608
Crystal sizes, mm	0.24 × 0.18 × 0.07
Range of data collection over θ, deg	2.16–30.84
Ranges of reflection indices	$-16 \le h \le 16$, $-14 \le k \le 28$, $-28 \le l \le 17$
Measured reflections	28246
Independent reflections	13608
Reflections with $I \ge 2\sigma(I)$	8999
Number of refines parameters	665
R_1, wR_2 ($I > 2\sigma(I)$)	0.0523, 0.1166
R_1, wR_2 (all reflections)	0.0879, 0.1406
GOOF (all reflections)	1.017
Residual electron density (max/min), e/Å^3	0.821/–1.040

In crystals of complex **I**, the nickel(II) metallocenters are joined into tetrahedra (Ni...Ni 3.144–3.201 Å) and supplemented to the distorted cubane cage Ni_4O_4 by the μ_3-bridging oxygen atoms of the hydroxy groups (Scheme 1, Fig. 3). In turn, the coordination environment of each of four nickel metallocenters is a distorted tetrahedron. Four nickel atoms exist in the same coordination environment formed by three donor atoms of one molecule of deprotonated ligand L. The equatorial plane is formed by the nitrogen atom of the secondary amino group and the oxygen atoms of the sulfo group of the ligand and two bridging hydroxy groups. The oxygen atom of the third bridging hydroxy group and the nitrogen atom of pyridine of the same ligand lie on the axial axis. The main characteristics of one coordination mode are given in Table 2. Thus, each organic ligand L is tridentate (Scheme 1, Fig. 4), exists in the facial conformation, and forms two conjugated six-membered chelate cycles: one chelate of the NiNN type, and another chelate cycle of the NiNO type. The tetranuclear structure is stabilized by numerous intermolecular interactions and intramolecular π–π stacking of the aromatic rings of the organic ligand. The fragment of the crystal packing of complex **I** is shown in Fig. 5. The distances between the centers of the aromatic rings are 3.703 and 3.880 Å.

In the literature among several other known homometallic nickel(II) complexes involving N-substituted taurine derivatives, complex **I** is the second example of cubane complexes along with complex **II** synthesized from the previous homological ligand *N*-2-(2-pyridyl)methyl-2-aminoethanesulfonic acid [8]. The chemical structures of cubane complexes **I** and **II** are similar. The ligands exist in the facial conformation each forming two conjugated chelate cycles and perform the tridentate function. A comparison of the bonds shows that they are longer in complex **I** than in complex **II**, including the Ni–O bonds with the bridging hydroxy groups (Table 3). Thus, the transition from the five-membered chelate cycle NiNN in com-

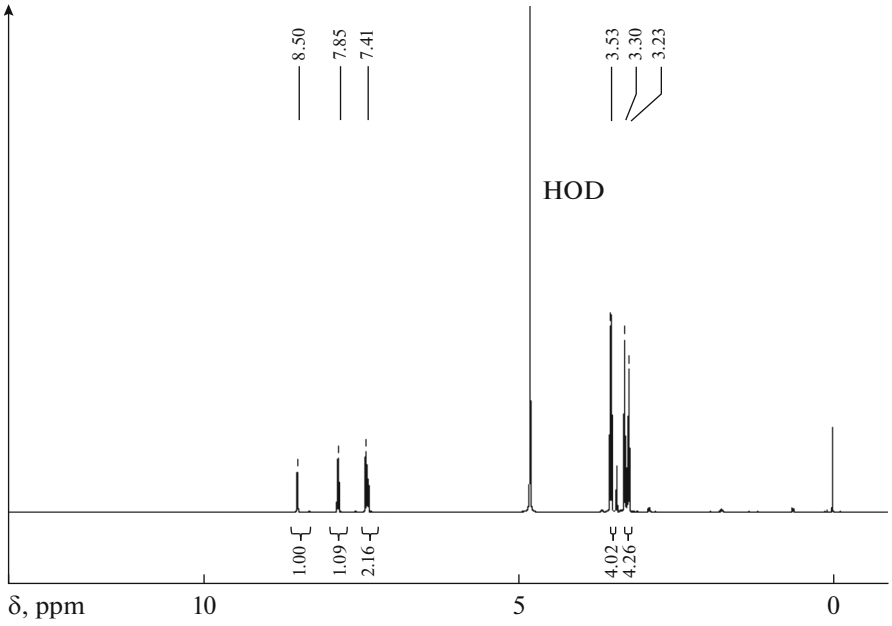


Fig. 1. ^{1}H NMR spectrum of ligand HL in D_2O (HOD is partially deuterated water).

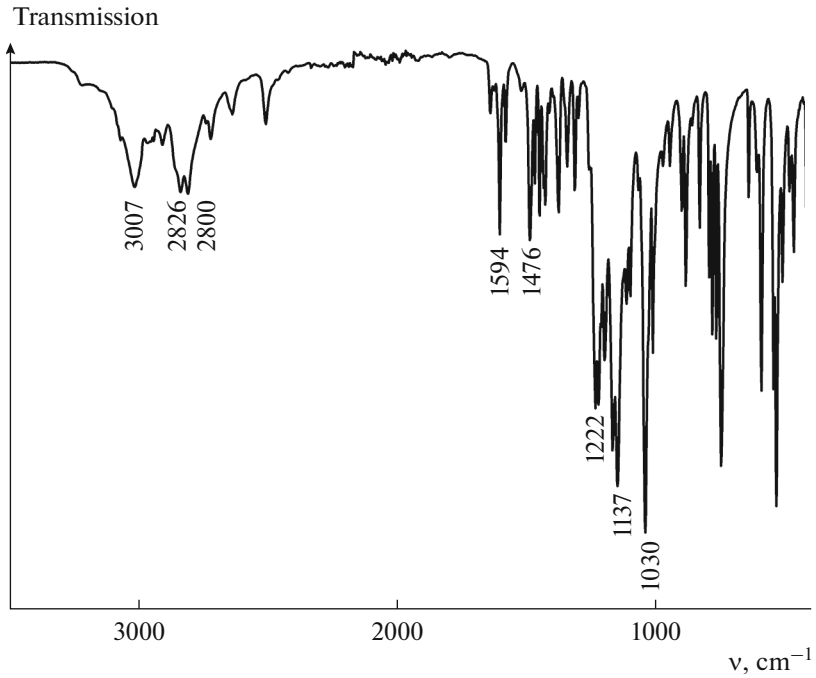


Fig. 2. FT-IR spectrum of ligand HL (ν, cm^{-1}): 3007 m ν(N–H), 2826 m, 2800 m ν(C–H), 1594 m δ(N–H), 1476 m δ(C–H), 1222 m ν(C–N), 1137 s, 1030 c ν(S=O).

plex **II** to the six-membered one in complex **I** demonstrates a decrease in the donor character of all denticities of both the ligand and bridging hydroxy groups. The donor character of the oxygen atom of the sulfo group is retained sufficient for the participation in the coordination sphere contrary to the nickel(II) complex based on *N*,*N*-bis(2-hydroxyethyl)taurine in which the sulfo group is not involved in coordination [3].

Additional distinctions of complex **I** from complex **II** are a lower number of solvate water molecules (Table 3) and different values of crystallographic parameters and space symmetry group (*C*2/*c* for com-

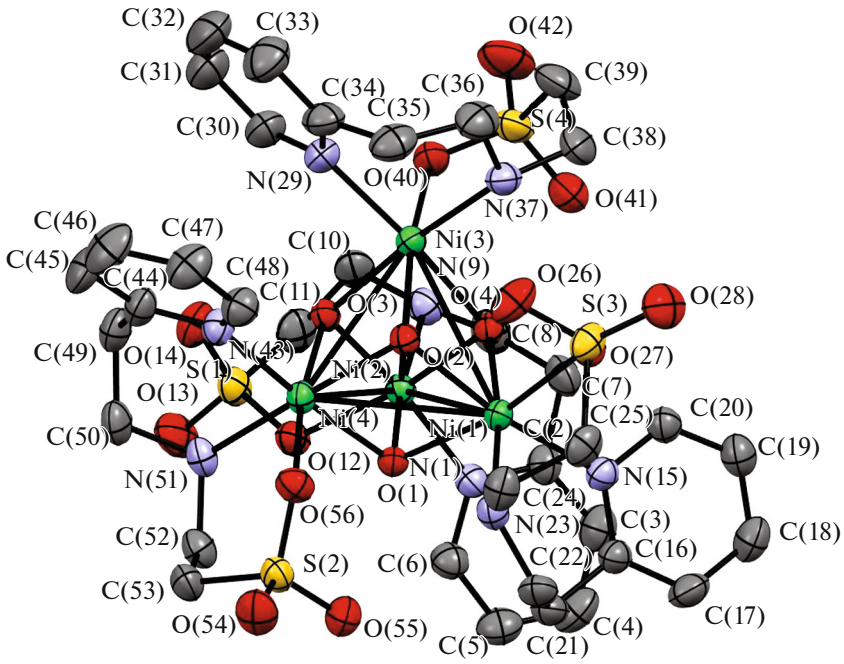


Fig. 3. Molecular structure of complex **I** in thermal ellipsoids of 50% probability. Hydrogen atoms are omitted.

plex **II**). The intercentroid distances between the pyridine rings involved in the π–π interaction for complex **II** are 4.578 and 3.949 Å, and those for complex **I** are 3.703 and 3.880 Å.

Thus, the preparation of the second cubane-like nickel(II) complex based on N-derivatives of taurine confirms the earlier found regularity of the influence of the ligand structure on the composition and structure of the formed coordination compound [1, 5]. In fact, an increase in the denticity and steric hindrances

Table 2. Selected bond lengths (Å) and bond angles (deg) in the coordination mode of complex **I**

Bond	*d*, Å	Angle	ω, deg
Ni(1)–O(1)	2.101(3)	O(1)Ni(1)O(27)	167.46(10)
Ni(1)–O(2)	2.090(3)	O(1)Ni(1)N(15)	106.74(11)
Ni(1)–O(27)	2.144(3)	O(1)Ni(1)N(23)	91.54(10)
Ni(1)–N(15)	2.111(3)	O(2)Ni(1)O(1)	78.02(10)
Ni(1)–N(23)	2.143(3)	O(2)Ni(1)O(27)	89.57(10)
Ni(1)–O(4)	2.047(2)	O(2)Ni(1)N(15)	170.80(10)

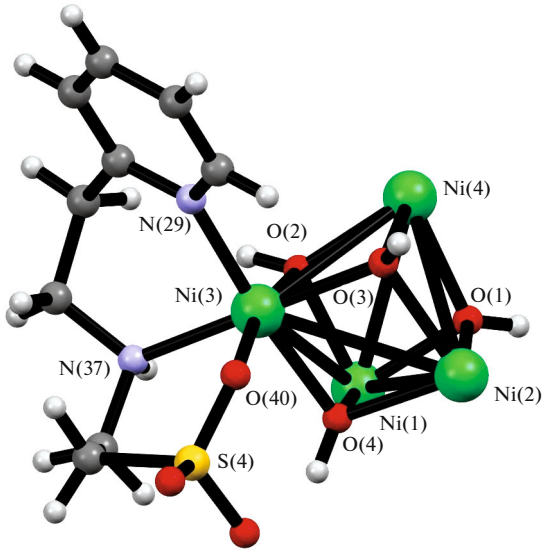


Fig. 4. Coordination environment of the metallocenter in complex **I** according to the XRD data.

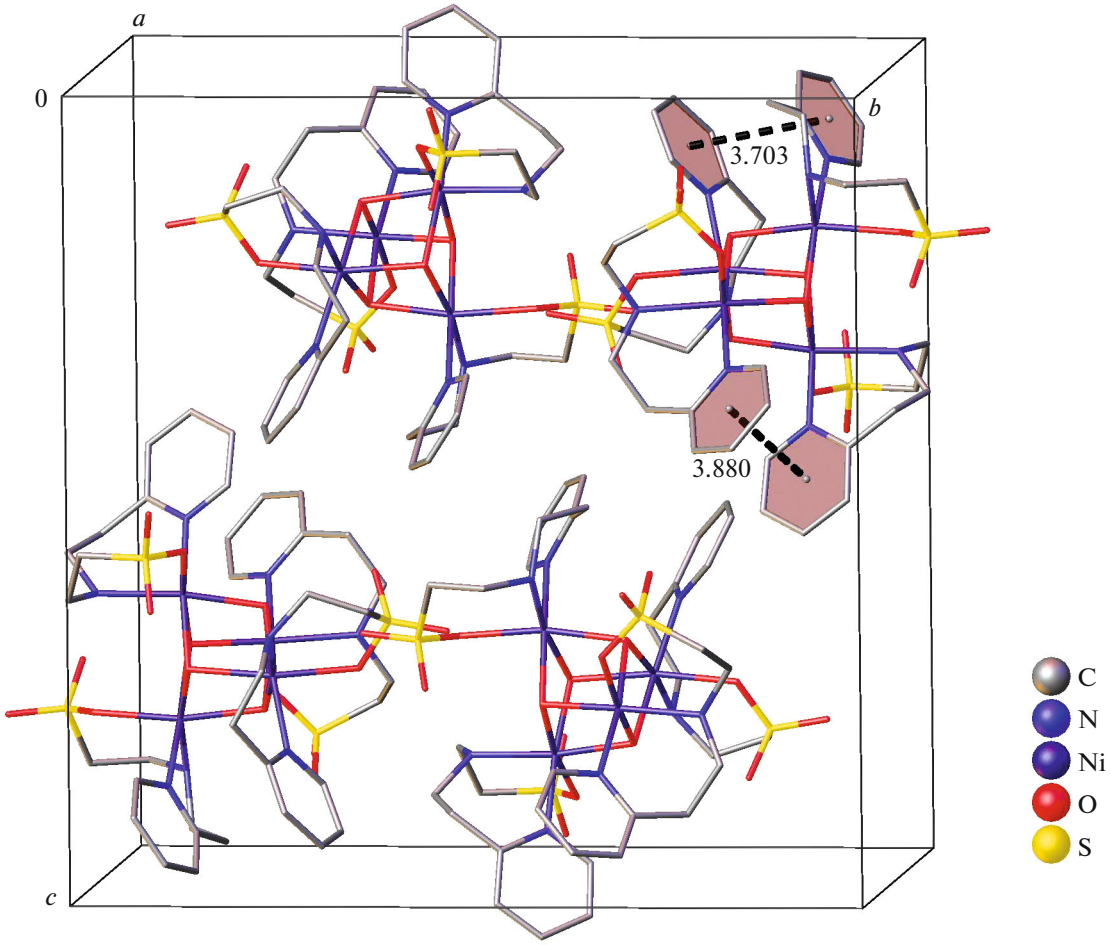
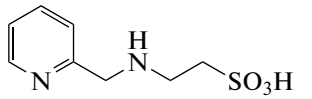
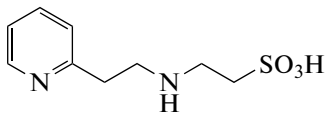


Fig. 5. Fragment of the crystal packing of complex **I**. The distance is given in Å.

of the amino group in the series of N-derivatives of taurine, as for the β-alanine derivatives, favors the formation of oligonuclear coordination compounds. As a result, the N-derivatives of taurine are promising chelating ligands due to such advantages as a relatively simple chemical structure and the use of simple methods of organic synthesis for the preparation of compounds. This provides commercial availability of the

Table 3. Minimum and maximum bond lengths in the coordination mode of the cubane nickel(II) complexes in the series of the taurine derivatives

Ligand HL	Coordination compound	Bond length, Å				Literature
		Ni–OH	Ni–O	Ni–N	$Ni–N_{pyridine}$	
	$[Ni_4L_4(OH)_4]\cdot 8H_2O$	2.038 2.072	2.125 2.129	2.089 2.106	2.062 2.089	[8]
	$[Ni_4L_4(OH)_4]\cdot 2H_2O$	2.046 2.106	2.130 2.147	2.118 2.142	2.078 2.111	This work

compounds and a possibility of the target variation of the ligand structure for the synthesis of required complicated coordination compounds.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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